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**EXTRACTION AND REFINING OF RUTIN FROM GREEN BUCKWHEAT**

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## I. INTRODUCTION

Three methods for the extraction of rutin from buckwheat have been developed at this Laboratory: (1) solvent extraction of green plant, (2) dilute alcohol extraction of buckwheat leaf meal, and (3) hot water extraction of buckwheat leaf meal. The first method has been described only briefly in a previous publication,<sup>1</sup> while the latter two have been described in detail.<sup>2</sup> Improvements have been made in all three of these processes since these publications appeared. The purpose of the present Circular is to describe the improved method for extracting and purifying rutin from the green plant. Improvements in the methods dealing with buckwheat leaf meal will be described in a forthcoming publication.

Extraction of green buckwheat has the advantage of simplicity and efficiency, since drying of the plant and losses of rutin in the drying process are avoided.<sup>2,3</sup> The method, however, has the obvious disadvantage that the operations are seasonal, and extraction schedules may be subject to restrictions imposed by weather and optimum time of harvest. The crude rutin, however, is quite stable and may be accumulated and refined as convenient after the extraction season is over.

High yields of rutin from green buckwheat will be obtained only by proper attention to critical factors such as age at harvesting, handling of the harvested plant, time elapsed between harvesting and immersion in solvent, ratio of solvent volume to plant weight, and efficient filtration during refining.

The maximum yield, on the basis of rutin per acre, is obtained when the buckwheat is harvested at full bloom before the seeds have set, roughly 28 to 35 days after sprouting in the case of the Japanese variety, *Fagopyrum esculentum*.<sup>3</sup> Preliminary data indicate that the tartary variety (duckwheat), *F. tataricum*, is superior to the Japanese for rutin production, since it has a substantially higher rutin content, maintains its high rutin content for a longer period, and is more frost-resistant. This variety should be harvested about 35 to 50 days after sprouting. Since buckwheat stems contain little rutin, relatively heavy planting and high mowing may be advantageous. Large losses of rutin will occur if the plants are bruised or crushed, or if more time than 24 hours elapses between harvesting and immersion in solvent.

The extraction procedure described applies to use of strong ethanol or denatured ethanol as a solvent. Experiments indicate that isopropanol or methanol are equally satisfactory. The equipment required may be similar to that outlined for the extraction of buckwheat leaf meal with dilute alcohol.<sup>2</sup> Contact of liquors with iron, copper, and aluminum must be avoided.

<sup>1</sup> J. F. COUCH, C. F. KREWSON, J. NAGHSKI, AND M. J. COPLEY, BUR. AGR. AND INDUS. CHEM. AIC.115, APRIL 1946, "THE CHEMISTRY AND THERAPEUTIC USE OF RUTIN."

<sup>2</sup> R. K. ESKEW, G. W. M. PHILLIPS, E. L. GRIFFIN, JR., AND P. W. EDWARDS, BUR. AGR. AND INDUS. CHEM. AIC.114, APRIL 1946, "PRODUCTION OF RUTIN FROM BUCKWHEAT LEAF MEAL."

<sup>3</sup> J. F. COUCH, J. NAGHSKI, AND C. F. KREWSON, SCI. 103, 197 (1946), "BUCKWHEAT AS A SOURCE OF RUTIN."

For the sake of clarity in applying or evaluating the method, the procedures for extraction of green buckwheat and for refining the rutin are outlined in the form of numbered steps. Detailed information and explanatory statements regarding the various steps appear in italics.

## II. EXTRACTION

1. Choose a tank made of stainless steel, wood, or glass, avoiding iron, copper, or aluminum equipment.

*It is important that iron, copper, and aluminum equipment be avoided in both the extraction and refining of rutin. Evidence indicates that these metals have the ability to form complexes with rutin which have similar solubility characteristics. Rutin so contaminated cannot be purified by the usual methods. Where iron is a contaminant the yield of purified rutin is known to be considerably less than normal. If purified rutin shows low transmittance in the visible spectrum after one recrystallization from water (using silica gel) and an isopropanol treatment the presence of iron, copper, or aluminum should be suspected. This may be confirmed by ashing a sample and applying the usual qualitative tests for these metals.*

*For removal of contaminating metallic impurities and acid-insoluble material, the following technique may be used: The rutin is dissolved in boiling water (pH 6 - 6.5) at the rate of one pound to 30 gallons of water. After cooling the solution to about 80° C., enough dilute sulfuric acid is added to adjust the pH to approximately 2.5. (It must be less than 3. About 2 ml. of 1 N sulfuric acid is usually required for each gram of rutin treated.) After stirring, this solution is allowed to stand for 10 to 15 minutes at 80° C. If no precipitate is observed, filtration is not necessary. If a precipitate is observed the solution should be allowed to stand at 80° C. for about one hour. There is danger of rutin precipitating if the solution is allowed to cool much below 70° C. If acid-insoluble materials agglomerate on standing, the solution is filtered prior to cooling in the usual manner for rutin crystallization. The rutin is filtered off after 20 hours and washed free of acid before drying.*

2. Fill the tank about one-fourth full with alcohol.

*Ethanol or denatured alcohol has been the solvent used in this Laboratory. It is believed that methanol and isopropanol may be used since these alcohols have been found satisfactory in the extraction of rutin from dried buckwheat leaf meal and have been used on a small scale in the laboratory for extraction of green plant.*

3. Add the green buckwheat (whole plant, less roots), packing it loosely. Submerge the plant completely, adding solvent and plant until the tank is filled. About 150 to 200 pounds of green plant can be conveniently packed in a 100-gallon tank and will require approximately 75 gallons of solvent.

*It is not necessary to cut the fresh green buckwheat into small pieces; it may be packed whole (less roots) into the tank. However, if the plant is cut, under no circumstances should it be minced or crushed. Optimum extraction of rutin*

from fresh green buckwheat takes place when strong alcohol is used to cover the plant. The concentration of alcohol in the extracts should preferably not fall below 70 percent by volume. If recovered alcohol of less than 90 percent strength by volume is used it will be necessary to increase the quantity above that specified so that the water present in the green plant will not dilute the alcohol below 70 percent.

4. Allow plant to macerate 12 to 24 hours.

5. Draw off and filter the extract and replace with fresh strong solvent.

*The first extract may be held in storage to be combined with the second extract for evaporation, or may be concentrated to about one-third volume and held until the second extract is available.*

6. Allow 12 to 24 hours for maceration.

7. Draw off and filter the second extract and wash entrained extract out of the marc with several portions of fresh solvent.

*After the second extract is withdrawn from the plant, the marc should be washed three times if complete removal of entrained solution is desired. Recovered solvent may be used for this purpose. Washings may be used to make second extraction of new plant if the solvent used for washing is stronger than 80 percent. Alcoholic extracts containing rutin should not be allowed to stand for long periods (one week or longer) before they are worked up for rutin.*

8. Distill off the solvent completely from the combined extracts.

*It is desirable that complete removal of solvent from the extracts be attained. This requires about a 90-percent reduction in volume. At this point the temperature of the distilling vapor will be approximately 208° F. Agitation is desirable in the final stage of evaporation of solvent, otherwise a "froth point" is observed where the volume has been reduced to about 70 to 80 percent of the original. Here the fats begin to separate out and agitation will break the foam, permitting a smooth and rapid completion of the evaporation.*

9. Draw the boiling concentrate from the evaporator to a steam-jacketed holding tank, straining off the fats through a glass-wool filter mat. Keep the concentrate boiling in the holding tank.

*The bulk of the fats will be removed from the boiling concentrate by straining through glass wool or similar material. A convenient strainer is constructed of coarse-mesh wire (1/2" mesh galvanized is suitable). This may be bent to form a rectangular box about 6 to 8 inches deep and of suitable length and width. The box is conveniently suspended across the top of a steam-jacketed holding tank between two wooden slats. In operation the box should be lined across the bottom and up the sides with several thicknesses of glass wool.*

10. Filter the boiling, strained liquid through a canvas-backed heavy filter-paper mat.

*About two to three square feet of canvas-backed heavy paper mat is required for each 10 gallons of concentrate filtered. (Republic Filter Corp. No. K-5 paper has been found satisfactory. However, the mention of commercial products does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.) Crude rutin properly strained and filtered by this operation contains less than 0.05 percent of fatty material. The evaporator and filtering equipment are usually washed with boiling water. The washings are kept separate from the main concentrate.*

11. Allow the filtrate to cool for rutin to crystallize. Running cold water through a jacketed tank facilitates cooling. After cooling, let stand about 20 hours. Avoid longer holding at room temperature; otherwise fermentation may occur.

12. Filter off the crude rutin in a filter press on hard-surfaced paper (sharkskin) or heavy canvas, and wash the crystals with a small quantity of cold water.

13. Remove crude rutin from the filter press and slurry it with a small quantity of cold water. Filter. Repeat, giving crude rutin at least three cold water slurries. Dry at 110° C.

### III. REFINING

#### (a) Recrystallization from Hot Water Using Silica Gel

14. Dissolve crude dry powdered rutin in boiling water. Use 20 gallons (cold measurement) of water to dissolve each pound of crude rutin.

*If tap water is used the water must be boiled; the pH after boiling for 10 minutes should not exceed 8.5. Adjust with sulfuric acid if necessary. In some localities where bicarbonates are present in the water the pH increases as the water boils and the water becomes alkaline. Alkali will hydrolyze rutin solutions.*

15. Filter the boiling solution through a canvas-backed heavy filter mat. One square foot of filtering area for each pound of crude rutin is sufficient.

*Hot-water-insoluble impurities must first be removed by filtration before treatment with silica gel (step 16) in order not to foul the gel. To facilitate filtration, filter-aid may be added after the rutin is dissolved. Two to three ounces of infusorial earth for each pound of rutin has been found adequate. Alkaline materials must be avoided.*

16. To the boiling filtrate in a jacketed holding tank add silica gel in the proportion of one-half pound of 20-65 mesh per pound of crude rutin. Stir and boil 10 minutes. During the entire crystallization keep the water volume constant by addition of water.

*The purpose of silica gel is to remove so-called "red pigment." The addition of silica gel to a boiling solution must be done carefully to avoid frothing over. It is usually advisable to turn off the steam during this addition. Continued stirring is required to keep the silica gel from falling to the bottom of the container and clogging the outlet valve.*

17. Filter the resulting rutin solution through clean canvas-backed heavy paper mat. One square foot of filtering area is required per pound of rutin refined.

18. Allow rutin to crystallize from filtrate as suggested in step 11.

19. Filter off rutin and dry to constant weight at 110° C.

*If the crude rutin is properly slurried and the filtrations at all stages are adequate, the refined rutin will be sufficiently freed of extraneous material to render it of pharmaceutical purity. Otherwise, removal of alcohol-insoluble material will be necessary.*

#### (b) Removal of Alcohol-Insoluble Material

20. Dissolve thoroughly dried powdered rutin in boiling isopropanol (98-99 percent) at the rate of one pound per 1-3/4 gallons of solvent (solvent measured cold).

*Ethanol and methanol are less satisfactory than isopropanol for removing alcohol-insoluble material. The quantity of material removed from rutin by filtration from a methanol solution is considerably less than from an ethanol solution. More extraneous material is removed by cooling the solution before filtration. However, if cold filtration of methanol or ethanol solutions is attempted, rutin is likely to precipitate before filtration is completed. In any case the alcohol used should be anhydrous and the rutin thoroughly dried and powdered before dissolving. If ethanol is used as a substitute for isopropanol for removing alcohol-insoluble material, the rutin is dissolved at the rate of about one pound to each 2-1/2 quarts of solvent. The solution should be filtered hot through heavy paper. The filtrate is then poured into 10 volumes of cold water and allowed to stand 24 to 48 hours for rutin to crystallize.*

21. Concentrate the isopropanol solution to half volume. Cool to room temperature. Filter off insoluble material using heavy paper. Wash with small portions of cold isopropanol.

22. Pour the filtrate and washings into 10 volumes of cold water.

23. Allow to stand at least 24 hours for rutin to crystallize. Filter. Dry at 110° C.